METAL FINE PARTICLE-CONTAINING FIBER AND ITS PRODUCTION

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Abstract of **JP9241970**

PROBLEM TO BE SOLVED: To obtain a fiber imparted with functions such as antibacterial, antifungal, deodorizing properties, etc., which are inherent to metal fine particles by depositing specific metal fine particles in a porous fiber having polar groups capable of ion exchanging or ion coordinating, and cross-linking structures. SOLUTION: This metal fine particle-containing fiber is obtained by forming a fiber of porous body from an acrylonitrile polymer having a hydrazine cross- linked structure, polar groups capable of ion exchanging or ion coordinating by converting >=0.1% of the residual nitrile groups into carboxyl groups and forming pores having <=0.85&mu m pore size, mutually connected and opened on the fiber surface, and ion exchanging or coordinating at least >= one metal ion selected from a group consisting of Ti, V, Cr, Fe, Mn, Co, Cu, Zn, Ag, Cd, etc., e.g. Ag ion, then depositing the metal fine particles by a reducing reaction.

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1]Metal particulate content textiles which contain metal particulates in textiles which have a polar group in which ionic exchange or ion coordination is possible, and have bridge construction structure, and are characterized by things.

[Claim 2][metal particulates] Ti, V, Cr, Fe, Mn, Co, nickel, Cu, Zn, Ga, germanium, Se, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, The metal particulate content textiles according to claim 1 being one or more sorts chosen from a group of Bi.

[Claim 3]The metal particulate content textiles according to claim 1 or 2 textiles which have bridge construction structure becoming by a porous body in which a pole diameter has fine pores of 0.85 micrometer or less, and connecting these fine pores, and carrying out free passage puncturing in a fiber surface.

[Claim 4]The metal particulate content textiles according to any one of claims 1 to 2, wherein textiles which have bridge construction structure become by a bridge construction acrylonitrile series polymer by hydrazine bridge construction and 0.1% or more of residual nitrile groups of this polymer are changed into a carboxyl group.

[Claim 5]The metal particulate content textiles according to claim 1 or 2, wherein textiles which have bridge construction structure become by a polymer which has the feature according to claim 4 and this polymer becomes by a porous body which has the feature according to claim 3.

[Claim 6]A manufacturing method of metal particulate content textiles making metal particulates a metal ion deposit in bridge construction textiles by a reduction reaction immediately to a polar group in bridge construction textiles containing a polar group in which ionic exchange or ion coordination is possible ionic exchange or after carrying out ion coordination.

[Claim 7][metal particulates] Ti, V, Cr, Fe, Mn, Co, nickel, Cu, Zn, Ga, germanium, Se, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, A manufacturing method of the metal particulate content textiles according to claim 6 being one or more sorts chosen from a group of Bi.
[Claim 8]A manufacturing method of the metal particulate content textiles according to claim 6 or 7 textiles which have bridge construction structure becoming by a porous body which has fine pores with a pole diameter of 0.85 micrometer or less, and connecting these fine pores, and carrying out free passage puncturing in a fiber surface.
[Claim 9]A manufacturing method of the metal particulate content textiles according to claim 6 or 7, wherein textiles which have bridge construction structure become by a bridge construction acrylonitrile series polymer by hydrazine bridge construction and 0.1% or more of residual nitrile groups of this polymer are changed into a carboxyl group.
[Claim 10]A manufacturing method of the metal particulate content textiles according to claim 6 or 7, wherein textiles which have bridge construction structure become by a polymer which has the feature according to claim 9 and this polymer becomes by a porous body which has the feature according to claim 8.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to metal particulate content textiles and its manufacturing method. Various functions which metal particulates originally have by containing metal particulates in textiles, For example, antibacterial properties, mildewproof capability, deodorization nature, fire retardancy, ultraviolet-rays prevention, thermal storage nature, It can be considered as the textiles which have functions, such as the improvement of surface nature, grant of design nature, grant of coolness, conductivity, rust prevention, lubricity, magnetism, light reflex nature, optical selective absorption, heat absorption, heat conduction, and a thermal reflex, and it becomes possible to use for the various fields which can utilize these functions.
[0002]
[Description of the Prior Art]The textiles which have conventionally various functions for which the diameter of a particle contains the metal particulates below a micron order grade in a textiles matrix are proposed. As most general thing, metal particulate content textiles have been obtained by adding the metal particulate itself in polymer and fibrosing after distribution as JP,H1-96244,A, JP,H2-16940,A, JP,H6-293611,A, etc. see. Inorganic particulates were made to support metal particulates so that JP,H7-165519,A, JP,H7-173392,A, etc. may see, and metal particulate content textiles have been obtained by adding and fabricating this

inorganic particulate in resin. However, it is difficult to distribute metal particulates or inorganic particles uniformly in polymer in these methods according to the difference of the specific gravity of metal particles or inorganic particles, and polymer, or the defect of compatibility. The metallic powder below a submicron is difficult to produce among the metal particulates added in these methods, it will become high also in cost and there is a problem that handling safe again is difficult. Therefore, a limit is among the diameters of a particle of the metal particulates which can actually be used industrially. In these forming processing processes, a heat history is received in many cases, and there is also a problem that the metal itself denatures in that case.

[0003]In JP,H6-287355,A and JP,H6-293611,A, after making metal salt etc. contain in the polymer which is the mother's body, it is considered as forming objects, such as textiles, by returning metal salt by heat-treatment by considering it as the resin which contained the ultrafine particle uniformly, and fabricating this. However, these methods include the following problems. 1. Uneven distribution may be produced in the stage of mixture with a metal complex or metal salt, and polymer materials. 2. The cost of a metal complex or metal salt itself is high. 3. The compound in which at least ** of a metal complex has the counterion of the metal ion of a child or a metal salt compound turns into discard, after a metal complex or metal salt is changed into metal particulates. Since elution etc. take place, these discard is ****** about influence to a basic property, other substances, etc. 4. Since the compound in which at least ** of a metal complex used as discard has the counterion of the metal ion of a child or a metal salt compound after a metal particulate deposit is included so much, content of metal particulates cannot be made not much high. 5. In the case of the former cited invention, since a matrix is thermoplastics which can carry out hot forming processing, what is excellent in heat resistance is not obtained.

[0004]In JP,S56-148965,A, although the silver particulate content textiles which contain metal silver in a textiles layer part are indicated, it has the problems following also in this case. 1. In order to prevent a textiles physical-properties fall, the quantity of the polar group which is making the portion with a textiles layer part small as much as possible localize carboxylic acid, and can support metal for this reason decreases, and the quantity of the metal particulates which can be contained in connection with it has a limit. 2. In the textiles generally obtained industrially, that fiber diameter is not less than about 10micro, for this reason, the surface area per unit weight is small, and when you are going to make it reveal the function of metal particulates, functional revelation efficiency is bad. The metal particulates of insides other than a layer part are effectively unutilizable. Since there is a problem like these [1 and 2], when it is going to use a metaled function, for example a lot of metal, such as anti-mold, is needed, it is necessary to raise the amount of addition of the metal particulate content textiles themselves, and a blending ratio to a degree very much, and, for this reason, becomes what

has high cost. Since the quantity of the metal itself is not enough, the target function may be unable to be revealed. 3. Since metal particulates localize and are only in a layer part, when it is comparatively mild conditions, it is satisfactory, but when mechanical friction [as / in post-processing] etc. are received, the surface is worn, and metal particulates drop out, and cause a functional fall remarkably. 4. Since silver ion by which ionic exchange was carried out is once used as silver compound, deposit precipitation is carried out and reduction reaction is performed after that, In order that a silver compound may deposit out of a system, and may reduce the utilization efficiency of a silver ion and may react in two steps in the case of a silver compound deposit, for this reason, a process becomes complicated and is disadvantageous in cost.

[0005]

[Problem to be solved by the invention]This invention is the textiles containing metal particulates, is excellent also in cost also in manufacture, and makes it a technical problem to provide the manufacturing method of the metal particulate content textiles which do not have the problem that the above old art saw, and these textiles.

[0006]

[Means for solving problem]this invention person has continued research wholeheartedly about the textiles containing metal particulates, and its manufacturing process. As a result, by making metal particulates contain in bridge construction polymer containing the polar group in which ionic exchange or ion coordination is possible, it finds out that the above-mentioned technical problem is solvable, and came to complete this invention. That is, this invention is metal particulate content textiles which contain metal particulates in the textiles which have the bridge construction structure containing the polar group in which ionic exchange or ion coordination is possible.

[0007]In a metal ion, the metal particulate content textiles of this invention are attained by the polar group in the bridge construction textiles containing the polar group in which ionic exchange or ion coordination is possible by the method of making metal particulates depositing in bridge construction textiles by a reduction reaction, ionic exchange or after carrying out ion coordination.

[0008]

[Mode for carrying out the invention]This invention is explained in detail below. First, by an application concerned, the textiles or the polymer (or polymer) which has bridge construction structure is called bridge construction textiles or a bridge construction polymer (or polymer) depending on the case, and when emphasizing the form, "textiles" uses "a polymer or polymer", when not asking a form. [as a polar group contained in the bridge construction polymer used for this invention] If it is ionic exchange or a polar group which can carry out ion coordination, there will be no limitation in particular the ion of an anion or a cation, and for

example, A carbonyl group, the 1st class amino group, the 2nd class amino group, the 3rd class amino group, the 4th class amino group, a phosphate group, a phosphoester group, a hydroxyl group, a mercapto group, a carboxyl group, an ether group, an ester group, a sulfonic group, a sulfonyl group, a sulfate ester machine, a cyano group, etc. are raised. A result with a good case where a carboxyl group, a sulfonic group, the 1st class amino group, the 2nd class amino group, the 3rd class amino group, the 4th class amino group, a phosphate group, and a cyano group are used is obtained, and the carboxyl group which is easy to form especially a metal ion, a complex, or salt is especially excellent.

[0009]As ion, limitation in particular does not have at least counterion or ** of a polar group which a polymer matrix of metal particulate content textiles of this invention has and in which ionic exchange or ion coordination is possible, and it can be suitably chosen according to the use. And this invention can be made more useful by a method of making antibacterial properties get impudent [antibacterial properties] and give by using a compound which at least the counterion or ** can also give a function to ion, for example, has the 4th class cation machine as counterion.

[0010]Although it can choose suitably as a quantity of a polar group to contain according to quantity of metal particulates which should be made to contain, since it becomes the quantity which deducted a polymer portion which forms a frame, it becomes 32 or less mmol/g. it is necessary to increase quantity of a polar group as much as possible, and a polar group of at least 1 or more mmol/g is included from on the other hand it being necessary to fully reveal a function of metal particulates in fact -- this -- better -- **. There is no restriction in particular also in an introducing method of a polar group to inside of polymer, and methods, such as introduction of a polar group by chemical and physical denaturation, can be used after introduction by using a monomer with a polar group in a polymerization stage of frame polymer, or frame polymer formation.

[0011]As a basic frame of polymer used as the matrix used for this invention, in the limitation which has bridge construction structure, it may be any of natural polymer, semisynthesis polymer, and synthetic polymer, and there is no restriction in particular. As concrete polymer, for example Polyethylene, polypropylene, VCM/PVC, ABS resin, nylon, polyester, a polyvinylidene chloride, Polyamide, polystyrene, PORIASE tar, polycarbonate, an acrylic resin, A fluoro-resin, a polyurethane elastomer, a polyester elastomer, Melamine resin, urea resin, polytetrafluoroethylene resin, unsaturated polyester resin, Plastics, such as an epoxy resin, urethane resin, and phenol resin; Nylon, Polyethylene, rayon, acetate, acrylics, polyvinyl alcohol, Textiles, such as polypropylene, cuprammonium rayon, bird acetate, and BINIRIDEN; Crude rubber and silicone rubber, SBR (styrene-butadiene rubber), CR (chloroprene rubber), Synthetic rubbers, such as EPM(ethylene-propylene rubber) FPM (fluorocarbon rubber), NBR (nitrile rubber), CSM (the Krol sulfonation polyethylene rubber), BR (butadiene rubber), IR

(synthetic natural rubber), IIR (butyl rubber), urethane rubber, and acrylic rubber, etc. are raised.

[0012]The characteristic of being able to be equal to physical and chemical change by which it is accompanied when compounding metal particulates especially, Namely, polymer with [from a heat-resistant and chemical-resistant point] a ****** basic frame to carbon-carbon combination, For example, vinyl system polymer is preferred and a good result can be obtained the polymer which can introduce easily especially the polar group in which ionic exchange or ion coordination is possible, and by specifically using the polymer of a polystyrene system, an acrylic ester system, and a polyacrylonitrile system.

[0013][as a structure of the bridge construction in the basic frame polymer which constitutes the textiles of this invention] The limitation in particular may not be in the limitation which does not receive denaturation physically [this polymer] and chemically in the process which makes metal particles contain, and the thing of which structure may be used for bridge construction by bridge construction by a covalent bond, ion bridge construction, a polymer intermolecular interaction, or a crystal structure, etc. Also in the method of introducing bridge construction, although there is no limitation in particular, since it is necessary to form textiles, it is necessary to carry out after fabricating for textiles.

[0014]Using a polyacrylonitrile system polymer, what introduced the bridge construction structure by hydrazine as a bridge construction structure is chemically and physically stable, and its textiles physical properties are good, it can raise the content of metal particulates, is excellent in heat resistance, and can obtain a result good also in cost. the case where the increase in nitrogen content is especially based on the hydrazine bridge construction which is 1.0 to 15.0 weight % -- further -- this -- better -- ****** can be obtained.

[0015]There is no restriction in particular in the limitation which the shape of a polymer matrix frame can hold also in the physical and chemical reaction accompanying metal fine particle formation also about the degree of bridge construction which is a rate of the bridge construction structure in a polymer matrix frame.

[0016]If it is the metal which deposits metal by a reduction reaction as a metal which is the particulates in this invention, there will be no limitation in particular, but, [the metal and the concrete target which are used for reactions, such as plating,] . [one or more sorts chosen from the group of Ti, V, Cr, Fe, Mn, Co, nickel, Cu, Zn, Ga, germanium, Se, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Hf, Ta, W, Re, Os Ir Pt, Au, Hg Tl, Pb, and Bi] Using is preferred. Considering it as the particulates of an alloy does not deviate from the range of this invention at all by using simultaneously two or more kinds in such metal. As a quantity of the metal to contain, it can set up arbitrarily in the level as which the function is required, and there is no limitation in particular.

[0017]Although the size of the metal particulates in this invention can be arbitrarily chosen

according to the use used and there is no limitation in particular, When it is a thing using the surface property of metal particulates, it is desirable at the point that the way of the smallest possible particles enlarges surface area, and the following [a submicron order of 1.0micro or less] are suitable. The design nature is used, or when using the volume, a certain amount of diameter of a particle is required, and a thing with a diameter of a particle of 10 micrometers or less is used preferably.

[0018]there is no limitation in particular as shape of the metal particulates in this invention -- a globular shape, a needle, a spindle shape, cylindrical [rod-like], the shape of a polyhedron, and multi-needlelike ** -- all shape can be taken. It can **, if there is no limitation in particular also as a state of distribution into bridge construction polymer and it chooses arbitrarily according to the use used. It has the feature that distributed support of this invention can be especially carried out completely uniformly over the whole textiles easily. However, methods, such as providing a concentration difference in the surface and the central part and considering it as domain structure, can also be taken, and such a method does not deviate from this invention at all, either.

[0019][as shape of the metal particulate content textiles in this invention] Although it is arbitrarily chosen according to the use used and there is no restriction in particular, since functional revelation ability is raised, surface area per unit weight can be enlarged, and a result with a good case of the textiles which are porous bodies can be obtained from the meaning of also using the metal inside textiles effectively. It is desirable, especially when it has a pole diameter of 0.85 micrometer or less, the fine pores connect and also it becomes a fiber surface especially from the porosity textiles which carry out free passage puncturing. In such a porous body, surface area is large, what also has the big degree of porous is more preferred, in fact, as for more than 1-m2/g, the degree of porous of surface area is more than 0.05-cm3/g, and a good result is obtained. However, while the physical properties of the textiles themselves fall that it is the thing that a pole diameter exceeds 0.85 micrometer, surface area decreases and a desirable result is not brought.

[0020]Surface area, the degree of porous, and the pole diameter used the mercury enclosure type porous degree measuring device, and the accumulation pushing volume (for the degree of porous) and accumulation surface area (for internal surface area) were calculated from the difference of a between with a pressure of 20,000 psi and 200 psi. This pressure range measures the pole diameter of 0.009 to 0.85 micrometer, considers that the surface of stoma volume / stoma is cylindrical shape, and measures it.

[0021]In the manufacturing process of this invention, it is made by making the compound which limitation in particular does not have in a polar group about ionic exchange or the method of carrying out ion coordination in a metal ion, and contained the metal ion in it contact the polymer matrix which has a polar group. Although an inorganic system or an organic

system may be sufficient as this compound containing a metal ion, a result with a good case where the compound of an inorganic system is used is obtained from the ease of carrying out of ionic exchange or ion coordination. There is no limitation in particular also as the method of contact with a polymer matrix, and it is made by the method of dissolving a metal ion in solvents, such as organicity or water, and contacting this to a polymer matrix.

[0022]If it is the method of returning a metal ion to metal as a reduction reaction method in the manufacturing process of this invention, there will be no limitation in particular. For example, sodium borohydride which is a compound which gives an electron to a metal ion, Hydrazine, formalin, the compound containing an aldehyde group, hydrazine sulfate, Hydrocyanic acid and its salt, hyposulfurous acid and its salt, thiosulfate salt, hydrogen peroxide, How to make it return in solution using reducing agents, such as a Rochell salt, grape sugar, a compound containing an alcohol group, hypophosphorous acid, and its salt, The method by heat treatment in the reducing atmosphere of hydrogen, carbon monoxide, hydrogen sulfide, etc., the method by light irradiation, or the method that combined these can be raised.

[0023]Into the system of reaction, the time of performing a reduction reaction in solution Sodium hydroxide, PH adjusters, such as basic compounds, such as ammonium hydroxide, inorganic acid, and organic acid, The thing or boron of a carboxylate salt system, such as sodium acid citrate and acetic acid sodium, Adding improvement agents, such as stabilizer, such as catalysts, such as buffers, such as alkali salt of inorganic acid, such as a carbonic acid, organic acid, and inorganic acid, a sulfide, and fluoride, a chloride, a sulfide, and a nitrification thing, and a surface-active agent, etc. does not deviate from this invention at all. In the case of the method by heat treatment in a reducing atmosphere, the same may be said of using nitrogen, argon, a helium, etc. together as inactive gas.

[0024]If it is the method of returning a metal ion ionic exchange or after carrying out ion coordination of depositing metal particulates to depend especially, as reductionism in the manufacturing method of this invention, there will be no limitation in particular, but. By carrying out ionic exchange of the metal ion, where a metal ion is fixed to the polar group in bridge construction textiles, a better result can be obtained by the method of performing a reduction reaction immediately. Although it is made to deposit into a polymer matrix once by using as metallic compounds the metal ion which carried out ionic exchange and there is generally also the method of making it change into metal particulates by a reduction reaction after that, When making it deposit into a polymer matrix as metallic compounds in the case of this method, metallic compounds' depositing easily out of a polymer matrix and the tendency same also at the time of a reduction reaction are accepted, and it is not economically desirable. It is thought that this phenomenon will happen since the size of the deposit compound accompanying a reaction changes and it shifts from the detailed hole of a polymer matrix. Preferably, using the method of this invention, it is a case where the reductionism by heat treatment is used, and the

metal ion which carried out ionic exchange in this case can be completely contained in bridge construction textiles, and a good result can be especially obtained from such a point.
[0025][about the number of times of operation of returning the above-mentioned metal ion ionic exchange or after carrying out ion coordination] When the quantity of the target metal particulates can make it contain, one operation may be sufficient, but. When the content of metal particulates needs to be increased, by repeating this operation and performing it, the method of obtaining the content of the metal particulates made into the purpose can also be taken, and a method can be suitably chosen according to the purpose used. In what is depended on the method of repeating especially, since the content of the metal particulates per unit polymer matrix weight can be increased, a desirable result may be given.
[0026]
[Working example]Although a work example explains this invention concretely below, this invention is not limited to the following work examples. As long as there is no notice, a weight standard shows the part and percentage in a work example.
[0027]AN system polymer which consists of work-example 1AN90% and 10% of methyl acrylate (henceforth MA) (ultimate viscosity in the inside of 30 ** JIMECHIRU formamide) [eta] = ****/wet bulb after carrying out silk thread spun and extension (a total draw ratio; 10 times) of the silk-thread-spun undiluted solution which dissolved 1.2l0 copy in 48% of RODAN soda water solution [90 copies of] in accordance with a usual state method = it dried under the atmosphere of 120 **/60 ** (14% of process contraction percentage), and the materials textiles Ia of single fiber ****** 1.5 g/d were obtained.
[0028]The materials textiles Ia were added in 10% hydrazine solution, and hydrazine crosslinking reaction was performed at 120 ** for 5 hours. It added in caustic-alkali-of-sodium solution 10% after a flush and drying, and the obtained bridge construction textiles carried out the hydrolysis reaction in 120 ** and 5 hours. The materials textiles Ib obtained after washing, drying, and dryness are 2.5% of a nitrogen increase of stock.
The amount of carboxyl groups was 4.2 mmol/g.

[0029]After adding the materials textiles Ib in 10% silver nitrate solution and carrying out an ionic exchange reaction for 80 ** and 30 minutes, the silver ion exchange processing textiles Ic were obtained after washing, drying, and dryness, and then heat treatment was carried out for 30 minutes at 180 **. As a result, the metal particulate content textiles Id of this invention which contained the silver particulates of 0.02 micrometer of mean particle sizes 6.5% were able to be obtained.
[0030]The work-example 2 silver-ion exchange processing textiles Ic were immersed in hydrazine fluid 10%, and the metal particulate content textiles IId of this invention were obtained by the same method as the work example 1 except having carried out reduction

processing for 20 minutes at 50 **.

[0031]Work-example 3 acrylonitrile / methyl acrylate / meta-ARIRU sulfonic acid soda = using AN system polymer produced by composition of 95/4.7/0.3, it dissolved in Rodin acid soda water solution 48%, and the silk-thread-spun undiluted solution was produced. Next, spin and rank second into 5 ** 12% Rodin acid soda water solution, and flush and 10 time extension are given, The porosity materials textiles IIIb with an average pole diameter of 0.04 micrometer were obtained by performing moist heat treatment using steam on condition of for [130 **x] 10 minutes, and also drying the obtained undried textiles for 20 minutes at 100 **. Next, these textiles were made to change into the metal particulate content textiles IIId by the same method as the work example 1.

[0032]. Mixed with 17.5 copies of glycerin, stirring 60 copies of work-example 4DMF in a container. Next, stirring 22.5 copies of acrylonitrile copolymers which consist of 5.7% of methyl acrylate, and 0.7% of sodium methallylsulfonate acrylonitrile 93.6%, it added and wrote and **** was continued at 80 ** for 1 hour. Next, after filtration, temperature of through and a silk-thread-spun duct was set as 180 ** for a silk-thread-spun cap with 500 holes, and the dry type silk thread spun of the solution was carried out by a usual state method. Viscosity of solution which has 22.5% of a solid content and 17.5% of a glycerin content is 85 fall ****, and is ******. Next, the obtained Towe was extended by a ratio of 1:3.6 by boil underwater, and where tension is applied slightly, boil underwater washed for 3 minutes. Subsequently, allowable contraction percentage l0%, in a screen drum drier, it dried at temperature of 100 **, and the porosity materials textiles IVb with an average pole diameter of 0.17 micrometer were obtained. Next, these textiles were made to change into metal particulate content textiles by the same method as a work example 1.

[0033]After carrying out hydrazine bridge construction of the materials textiles Ia obtained in work-example 5 work example 1 by the same method as a work example 1, washing, drying, and dryness were performed, and the materials textiles Vb for which a nitrile group remained were obtained, without carrying out hydrolysis processing. By the same method as a work example 1, you carried out silver ion exchange of the obtained textiles, and made it change into metal particulate content textiles of this invention by depositing silver particulates.

[0034]A characteristic value of textiles obtained by work examples 1-5 and an evaluation result are summarized in Table 1.

[0035]

[Table 1]

	実施例1	実施例2	実施例3	実施例4	実施例5
極性基	カルボキシル基	カルボキシル基	カルボキシル基	カルボキシル基	ニトリル基
極性基量	4.2mmol/g	5.1mmol/g	4.5mmol/g	4.8mmol/g	8.3mmol/g
細孔径			0.04 μm	0.17 μm	
表面積			55m²/g	25m²/g	
多孔度			0.2cm³/g	0.66cm³/g	
金属種類	Ag	Ag	Ag	Ag	Ag
還元法	熱	ヒドラジン	熱	熱	熱
金属含有量	15.0%	9.0%	11.0%	8.0%	3.0%
金属微粒子粒子径	0.02 μm	0.5 μm	0.01 μm	0.03 μm	0.01 μm
繊維強度	1.6g/d	1.5g/d	1.4g/d	1.5g/d	2.6g/d
繊維伸度	31%	18%	25%	28%	39%
結節強度	1.3g/d	1.0g/d	1.2g/d	1.4g/d	1.8g/d

[0036]Work examples 1-5 of this invention have textiles physical properties in which post-processing after spinning is possible, staple intensity, the degree of growth, and knot intensity as shown in Table 1.
And it is clear that very small metal particulates come to contain in high concentration, and metal particulates come to contain in work examples 3 and 4 in porous textiles.

[0037]Work examples 6-10 obtained metal particulate content textiles of this invention by the same method as a work example 3 except having changed a metal kind of metal particulates as shown in Table 2, and having changed a reducing agent. The physical properties of obtained textiles, the characteristic, etc. are united with Table 2, and are summarized.
[0038]
[Table 2]

	実施例6	実施例7	実施例8	実施例9	実施例10
金属塩水溶液	硫酸銅	硫酸ニッケル	塩化パラジウム	硫酸亜鉛	塩化第一錫+塩化ニッケル
金属種類	Cu	Ni	Pd	Zn	Sn/Ni
還元剤	ホルマリン	次亜リン酸	NaBH4	次亜リン酸	次亜リン酸
金属含有量	7.0%	3.5%	6.3%	2.9%	6.6%
金属微粒子径	0.3μm	0.1μm	0.4μm	0.05μm	0.05μm
単繊維強度	1.9g/d	1.8g/d	1.5g/d	1.9g/d	1.8g/d
単繊維伸度	27%	31%	20%	28%	31%
結節強度	1.6g/d	1.5g/d	1.1g/d	1.8g/d	1.6g/d

[0039]It is clear that various metal particulates contain in textiles of a porous body, and the physical properties of the textiles as well as Table 1 have textiles physical properties in which post-processing after spinning is possible, single fiber intensity, the degree of growth, and knot intensity in work examples 6-10 of this invention as shown by Table 2.

[0040]

[Comparative example 1] After heating the materials textiles Ia obtained in work example 1 for 20 minutes at 100 ** in 3% of caustic alkali of sodium, and hydrazine 0.01% of solution and bridge-construction-processing and hydrolysis processing, After washing and processing for 20 minutes at 100 ** by 0.5% of acetic acid solution subsequently, the materials textiles ib with a carboxyl group were obtained on the surface by washing and drying. After carrying out immersion treatment of these textiles for 10 minutes at 40 ** into 0.5% of silver nitrate solution, it washed and dried and the silver ion joint acrylic fibers ic which the silver ion combined were obtained. After these textiles immersed for 30 minutes at 70 ** into 0.5% sodium carbonate solution and deposited carbonic acid silver, it washed, dried and dried, and also the drying process of them was carried out for 30 minutes using a 130 ** hot air dryer, and they obtained the textiles id as a comparative example which contains silver particulates on the surface. The silver content of the obtained textiles was 1.5%, and the diameter of a particle of metal particulates was 0.05 micrometer. The result of having measured with the work examples 1 and 3 the silver concentration of silver ion exchange joint acrylic fibers in this case and the silver concentration in the silver particulate content unprocessed cotton finally obtained is shown in Table 3. Compared with the amount of silver ions by which ionic exchange was carried out in the method of depositing metallic compounds in textiles once and returning this, the silver concentration of final unprocessed cotton is falling below to half, and its utilization efficiency of a silver ion is not desirable in [it is bad and] cost as shown in Table 3. On the

other hand, in work examples 1 and 3 of this invention, the amount of silver ions by which ionic exchange was carried out contains in unprocessed cotton final as it is, and it has become what was excellent in the utilization efficiency of a silver ion.

[0041]

[Table 3]

	実施例1	実施例3	比較例1
Agイオン交換繊維中のAg含有量	15.0%	11.0%	3.2%
原綿Ag含有量	15%	11.0%	1.5%
編み地Ag含有量	14.0%	9.5%	0.02%

[0042]It knit by performing spinning and post-processing with 30% of the blended ratio using the unprocessed cotton of the work examples 1 and 3 and the comparative example 1, respectively, and the ground was created. In accordance with the result of having knit with the unprocessed cotton in that case, and having measured the silver content of the ground, it is shown in Table 3. In the comparative example 1, it knits and the silver content in the ground is falling extremely as shown in Table 3. Since the silver particulates which existed in the fiber surface separated and it fell by friction with metal, such as a guide, in subsequent processing processes as the spinner, this is considered. It is clear that such a state is not enough to use a metaled function and that it is very disadvantageous also in cost. On the other hand, although reduction of silver content is too accepted also in work examples 1 and 3, there are also silver contents of enough finally contained low, and they are practical. [of the rate of the reduction to the amount of whole]

[0043]Similarly paper making was performed for 130 g/m2 of metsukes using the unprocessed cotton of the work examples 1 and 3 and the comparative example 1. The materials composition of paper was carried out as it showed vinylon 1% and each unprocessed cotton in Table 4, and it created mixed papermaking by making the remainder into pulp. The obtained mixed papermaking molded by the wet process of JIS Z 2911, and estimated resistance as the bacillus pace of decrease of the pneumobacillus by the shake flask method. A bacillus pace of decrease shows the rate in which the bacilli to control decreased in number, and the one where this value is larger is excellent in antibacterial properties. Mold resistance is displayed by the following three ranks based on the result of having grown mold for 14 days.

1: Growth of sample area in which growth of mold 1/3Or more2: Molds does not accept growth of less than [1/3] 3:mold of sample area. [0044]

[Table 4]

	実施例 1 Id	実施例 1 Id	実施例 3 Ⅲd	実施例 3 Ⅲd	比較例 1 id	比較例 1 id
金属微粒子含有繊維混率%	2	10	2	10	10	50
肺炎桿菌菌減少率(%)	85	99.9	98.0	99.9	0.1以下	38
黴抵抗性	2	3	3	3	1	1

[0045]In the comparative example 1, an insufficient result is brought with antibacterial properties and mold resistance as it sees in Table 4. Since silver particulates exist only in a fiber surface, and this has too low the content of silver itself, it is considered to have brought such a result. Also in 50% of a blended ratio, the mold resistance of especially a silver quantity demanded so much is insufficient. If antibacterial properties and mold resistance raise the blended ratio, it will be thought that an effect improves, but it may become high in cost and practicality may be lost. On the other hand, in the work examples 1 and 3, it is admitted that antibacterial properties and antifungus are revealed even about 2% of addition. Since this has high silver concentration compared with a comparative example, it is considered that the function was revealed easily. In work example 3 which is especially porosity, the effect is remarkable and nearly perfect antibacterial properties and antifungus are revealed with the blended ratio 2%. That the silver particulates which contact the exterior when it became porosity and surface area increased increased by leaps and bounds, and since there are fine pores to the inside of textiles further, this is considered to be because for the quantity of the silver particulates which can carry out functional revelation to have increased substantially.

[0046]

[Effect of the Invention][the metal particulate content textiles of this invention] [by containing metal particulates in textiles] Various functions which metal particulates originally have, for example, antibacterial properties, mildewproof capability, It comes out to consider it as the textiles which have functions, such as the improvement of deodorization nature, fire retardancy, ultraviolet-rays prevention, thermal storage nature, and surface nature, grant of design nature, grant of coolness, conductivity, rust prevention, lubricity, magnetism, light reflex nature, optical selective absorption, heat absorption, heat conduction, and a thermal reflex. And since it can be considered as processed goods, such as paper, a nonwoven fabric, knitting, and textiles, by using the processability which was excellent in textiles, it becomes possible to use for the various fields which can utilize these functions.

[Translation done.]